DEGRADATION OF AZINPHOSMETHYL ON STONE FRUIT FOLIAGE, 1988

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SUMMARY

Three adjacent stone fruit orchards, two nectarine and one peach orchard, in Fresno County, California, were monitored for dislodgeable foliar residues of azinphosmethyl (O,O-Dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate) from May through August, 1988. The data was employed to describe the behavior of azinphosmethyl degradation and to estimate the half-life of the residues for each orchard. Replicate leaf disk samples were collected at selected intervals over the 12 week monitoring period and analyzed for azinphosmethyl residues and the oxygen analog (oxon). The mean initial deposition for all plots was 1.00 ug/cm^2 with a standard deviation (SD) of 0.22 ug/cm^2. Oxon residues were not detected until two weeks after application. The half-lives ranged from 26 to 32 days.

INTRODUCTION

Azinphosmethyl is a category I pesticide with an oral LD_{50} of 13 mg/kg and a dermal LD_{50} of 220 mg/kg (1). Azinphosmethyl is a broad spectrum phosphorodithioate organophosphate pesticide used primarily to control foliage feeding insects. Various application rates and dilutions are used to control coddling moth, oriental fruit moth and other important stone fruit pests. It is used extensively on hand harvested stone fruit, including peaches, apricots, nectarines and plums. These crops are propagated from the same rootstock and have similar cultivation, irrigation and harvest practices. This study monitored the degradation of azinphosmethyl dislodgeable foliar residues on nectarines and peaches. The reentry interval for these two crops is 14 days. The data provides a reference for the range of expected azinphosmethyl levels at various post-application harvest intervals. When correlated with estimates of dermal exposure while harvesting stone fruit, these data can serve as estimators for potential harvester exposure.

Sampling was conducted according to techniques adapted from those of Iwata et al. (2). Samples were analyzed for the parent compound and its oxon; the oxon was not detected until two weeks after application.

MATERIALS AND METHODS

With the assistance of the Fresno County Agricultural Commissioner, three adjacent stone fruit orchards (two nectarine, one peach) were selected and monitored during a 12 week period from May through August, 1988. All Guthion 35 WP (EPA number 3125-379) applications were made during the morning of May 25, 1988. The nectarine varieties were Del Rio Rey and Fairlane. The Del Rio Rey orchard was 9.5 acres and was treated at the rate of 0.7 lb/acre active ingredient (a.i.) in 20 gallons of water by electrostatic sprayer. The Fairlane orchard was 8 acres and was applied at the rate of 0.53 lb/acre a.i. in 250 gallons of water by an air blast sprayer. The peach orchard was 9.14 acres of Autumn Gem, treated at the rate of 1.4 lb/acre in 20 gallons of water by an electrostatic sprayer. All orchards were irrigated using a drip system.

Orchards were sampled according to the following scheme:

Four or five plots in each orchard were selected at random and marked with flagging tape. Beginning with the tenth tree in from the orchard border in each row, two leaf disks were collected from each of the next ten trees, using a 2.54 cm Birkestrand leaf punch fitted with a four ounce jar. The sample was completed by sampling the next ten trees in the adjacent row while exiting the orchard. A completed sample consisted of forty leaf disks. All leaf disks were collected from a height of approximately five feet. All orchards were sampled at 4 hours, 1 day, 2 days, and 6 days after application and then continued weekly for 7 weeks. Final sampling was conducted at 12 weeks post-application.

The jar containing the sample was sealed with aluminum foil, capped, sealed in a one gallon Ziploc^{R} plastic bag and stored in a styrofoam ice chest on ice. Samples were shipped to California Department of Food and Agriculture, Chemistry Laboratory Services in Sacramento for residue extraction within 24

hours. Samples were analyzed for dislodgeable residues of azinphosmethyl and its oxon. Residues were rinsed from the leaf surface using a 0.5 percent dioctyl sodium sulfosuccinate solution, then extracted from the aqueous solution with ethyl acetate and analyzed by gas chromatography.

One tank mix sample was drawn from the first tank mix prepared for each of the three orchards. These samples were stored in 0.5 liter Nalgene containers and placed immediately on dry ice and shipped to Chemistry Services for analysis.

Linear least squares regression was employed on the common log of the residue data versus time post-application to model an exponential decay curve. The exponential model was chosen so that the first-order half-life could be estimated. The half-life is an indicator of the rate of dissipation of a compound once it is applied to a leaf surface. The exponential decay model takes the following functional form:

$$y = B_0 10^{B_1 t}$$

where B_0 = initial deposition
B_1 = decay rate
and t = time post-application

The equation to determine the estimate half-life is:

$$t_{1/2} = \log (1/2)/ K$$

where K is the first order rate constant

RESULTS

The dislodgeable foliar residue results for each orchard are presented in Tables I-III. The mean and SD of the residues are reported in Table IV. For all orchards, the combined mean for initial deposition of azinphosmethyl was 1.00 ug/cm^2. The oxon was not detected in any sample until two weeks post-application. The mean residues for each orchard were below 1.00 ug/cm^2 by day 6 post-application. Although the application rates ranged from 1.5 lb/acre to 4 lb/acre and two different types of application equipment were used, the residue levels appear similar for all three orchards. The residue decay curves and estimated half-life for each orchard are presented in Figure I. The half-life for azinphosmethyl residues ranged from 26 to 32 days. The Del Rio Rey nectarine orchard had a residue half-life of 26 days. The Fairlane nectarine orchard had a residue half-life of 29 days. The peach orchard had the highest application of azinphosmethyl and has the longest half-life (32 days). The results of the tank mix analyses confirmed the application rates within 20 percent.

DISCUSSION AND CONCLUSIONS

The pattern of residue degradation is similar for all orchards, as illustrated in Figure I. Different application rates and methods between the orchards do not appear to effect great differences in initial deposition of azinphosmethyl, the residue degradation, or the estimated half-life.

Statistical differences in the half-lives were detectable at the $p = 0.05$ level, but the curves are so similar that the statistical difference in the resulting residues for any time interval is not likely to result in any practical or biological difference. The overall half-life for the three orchards is 27.5 days. The peach orchard (treated at 1.4 lb/acre by electrostatic sprayer) had the highest rate of application but did not have the highest dislodgeable residue. The peach orchard did have the slowest rate of residue degradation as evidenced by an estimated half-life of 32 days compared to 26 and 29 days for the nectarine orchards. The peaches are a late variety and the harvest was scheduled for either late August or early September. Nectarines mature earlier and are ready to harvest during July (weeks 7 - 10 of the study). Although no "safe work level" for azinphosmethyl residues has been established, harvest typically begins 1-2 months after application. Late varieties may be harvested three months after application. A harvester exposure study (HS-1532)(4) conducted in the Del Rio Rey orchard during week 7 post-application showed no depression of the blood cholinesterase levels of 18 workers. The current reentry interval (14 days) appears adequate, given the typical post-application harvest interval. The residue data presented here, when correlated with estimates of dermal exposures while harvesting stone fruit, can be employed to estimate potential harvester exposure over a 12 week post-application interval.

TABLE I

DISLODGEABLE FOLIAR RESIDUES OF AZINPHOSMETHYL APPLIED TO NECTARINES

NECTARINES, DEL RIO REY VARIETY
RATE: 2 lb/acre
APPLICATION DATE: 5-25-88

Azinphosmethyl (AZM) and azinphosmethyl oxon residues reported in ug/cm^2

REPLICATE	INTERVAL																		
	4 HR	DAY 1	DAY 2	DAY 6	1 WK.	2 WEEKS		3 WEEKS		4 WEEKS		5 WEEKS		6 WEEKS		7 WEEKS		12 WEEKS	
	AZM	AZM	AZM	AZM	AZM	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON
1	0.84	0.82	1.48	0.71	0.84	0.72	0.003	0.43	ND	0.37	ND	0.21	0.003	0.40	0.008	0.34	0.007	0.07	0.001
2	1.44	0.86	1.06	0.88	0.80	0.78	0.003	0.50	0.002	0.42	ND	0.29	0.006	0.49	0.009	0.26	0.007	0.07	0.001
3	1.10	0.86	1.12	0.94	0.87	1.11	0.005	0.44	ND	0.29	ND	0.32	0.004	0.35	0.005	0.38	0.009	0.14	0.002
4	1.27	0.70	1.12	0.81	0.88	0.79	ND	0.49	ND	0.30	ND	0.33	ND	0.39	0.006	0.18	0.004	0.05	ND
5	0.96	0.84	1.26	0.85	0.93	0.83	0.003	0.57	ND	0.47	0.007	0.28	ND	0.33	0.006	0.14	ND	0.16	0.004

No oxon was detected until day 14
ND: none detected, below 0.003 ug/cm^2

TABLE II

DISLODGEABLE FOLIAR RESIDUES OF AZINPHOSMETHYL APPLIED TO NECTARINES

NECTARINES, FAIRLANE VARIETY
RATE: 1.5 lb/acre
APPLICATION DATE: 5-25-88

Azinphosmethyl (AZM) and azinphosmethyl oxon residues reported in ug/cm^2

REPLICATE	INTERVAL																		
	4 HR	DAY 1	DAY 2	DAY 6	1 WK.	2 WEEKS		3 WEEKS		4 WEEKS		5 WEEKS		6 WEEKS		7 WEEKS		12 WEEKS	
	AZM	AZM	AZM	AZM	AZM	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON
1	1.03	1.10	1.44	0.87	0.90	1.09	0.008	0.68	0.005	0.50	0.006	0.40	ND	0.24	ND	0.37	0.009	0.09	ND
2	1.07	0.95	1.56	0.86	0.91	0.82	0.003	0.62	0.004	0.48	0.007	0.29	0.004	0.27	0.004	0.23	ND	0.12	ND
3	0.87	0.85	1.31	0.74	0.80	0.70	0.005	0.57	0.003	0.34	0.005	0.44	0.006	0.33	0.007	0.36	0.006	0.18	ND
4	0.90	0.81	1.19	0.70	0.82	0.62	0.005	0.65	0.004	0.45	0.009	0.41	0.008	0.42	0.009	0.49	0.011	0.18	ND

No oxon was detected until day 14
ND: none detected, below 0.003 ug/cm^2

TABLE III

DISLODGEABLE FOLIAR RESIDUES OF AZINPHOSMETHYL APPLIED TO PEACHES

PEACHES, AUTUMN GEM VARIETY
RATE: 4 lb/acre
APPLICATION DATE: 5-25-88

Azinphosmethyl (AZM) and azinphosmethyl oxon residues reported in ug/cm^2

REPLICATE	INTERVAL																		
	4 HR	DAY 1	DAY 2	DAY 6	1 WK.	2 WEEKS		3 WEEKS		4 WEEKS		5 WEEKS		6 WEEKS		7 WEEKS		12 WEEKS	
	AZM	AZM	AZM	AZM	AZM	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON
1	1.33	0.82	0.97	0.78	0.86	0.72	0.009	0.72	0.007	0.56	0.009	0.57	0.010	0.68	0.023	0.46	0.014	0.12	0.004
2	0.82	0.82	0.94	0.89	1.02	0.72	0.008	0.66	0.005	0.49	0.008	0.47	0.007	0.51	0.015	0.43	0.014	0.15	0.004
3	0.74	0.75	0.77	0.72	0.82	0.52	0.004	0.58	0.006	0.37	0.007	0.44	0.010	0.53	0.016	0.40	0.011	0.06	ND
4	0.90	0.75	0.91	0.74	0.94	0.74	0.006	0.51	0.003	0.48	0.007	0.43	0.096	0.49	0.015	0.38	0.094	0.05	ND
5	0.77	0.70	0.82	0.71	0.79	0.73	0.006	0.64	0.005	0.54	0.012	0.61	0.014	0.58	0.013	0.44	0.012	0.16	0.004

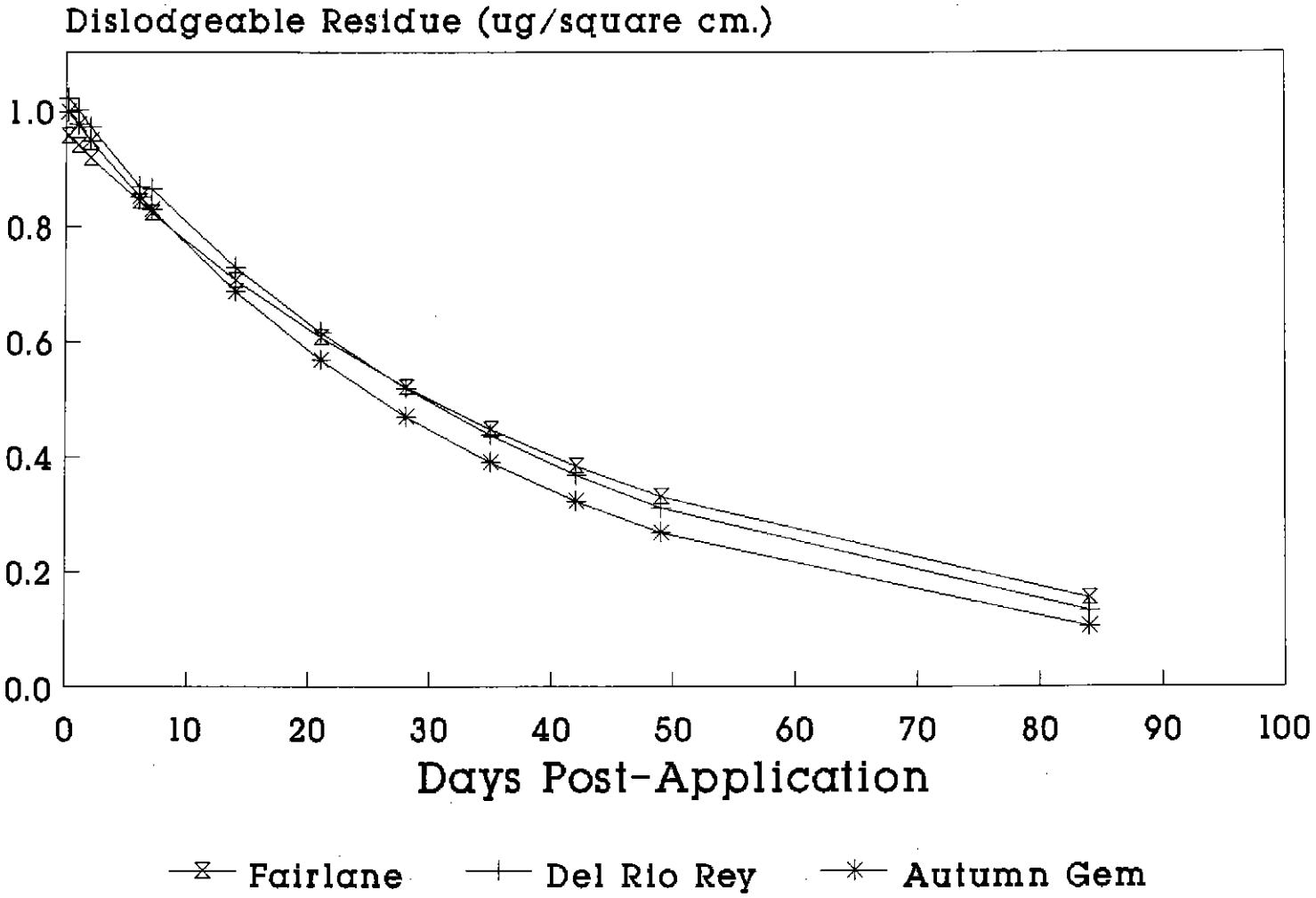
No oxon was detected until day 14
ND: none detected, below 0.003 ug/cm^2

TABLE IV

Means and SD of dislodgeable azinphosmethyl foliar residues on stonefruit (ug/cm^2)

	Del Rio Rey Nectarine		Fairlane Nectarine		Autumn Gem Peach	
Interval	Mean	SD	Mean	SD	Mean	SD
4 Hrs.	1.12	0.24	0.97	0.10	0.91	0.24
1 Day	0.82	0.07	0.93	0.13	0.77	0.05
2 Days	1.21	0.17	1.38	0.16	0.88	0.08
6 Days	0.84	0.09	0.79	0.09	0.77	0.07
1 Week	0.86	0.05	0.86	0.06	0.89	0.09
2 Weeks	0.85	0.15	0.81	0.21	0.69	0.09
3 Weeks	0.49	0.06	0.63	0.05	0.62	0.08
4 Weeks	0.37	0.08	0.44	0.07	0.49	0.07
5 Weeks	0.29	0.05	0.39	0.07	0.50	0.08
6 Weeks	0.39	0.06	0.32	0.08	0.56	0.08
7 Weeks	0.26	0.10	0.36	0.11	0.42	0.03
12 Weeks	0.10	0.04	0.14	0.05	0.11	0.05

Fig. 1 Azinphosmethyl Decay in Stone Fruit



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